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PHOTOCONDUCTIVITY OF UNDOPED ZNO THIN FILMS DEPOSITED BY SPRAY PYROLYSIS

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Résumé

Les couches minces d'oxyde de zinc ont été realises par spray pyrolysis. Nous nous sommes intéresseés à l'effet de la température, le temps dépôt sur les propriétés électriques, optiques et structurales. L'effet de la lumière sur l'augmentation de la conductivité des films est dû à l'absence d'oxygène. En coupant la lumière, nous remarquons une saturation de la photoconductivité attribuée aux pièges qui capturent les porteurs libres.

Mots clés : *photoconductivité, couches minces ZnO, spray pyrolysis, temps de dépôt, température de substrat, temps de relaxation, méthode de transformée de Laplace.*

Abstract

The photoconductivity of ZnO thin films prepared by spray pyrolysis of the zinc dihydrated were studied. The electrical, optical behaviors and structural spectra show an important effect of substrate temperature Ts and deposition time td. Under illumination, the conductivity of as-grown sample increased due to desorption of oxygen. A small photoconductivity is representative of the electrical behavior of a quasi intrinsic material. By following cessation of illumination, we remarked a saturation of decay photoconductivity, this can be attributed to traps which captures carriers.

Keywords: *Photoconductivity, ZnO thin films, spray pyrolysis, deposition time, substrate temperature, relaxation time, Laplace transform method.*

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ملخص

من خلال دراستنا،قمنا بتحضير رقائق اؤكسيد الزنك بطريقة الرش بيرولزي. تطرقنا الى اهمية درجة الحرارةTs و زمن الوضع td على الخصائص الكهربائية، البصرية و البنيوية. ينتج عن اثر الضوء ازدياد في الناقلية الكهربائية بسبب امتصاص الاكسجين من طرف الرقائق. هذه القياسات سمحت لنا بحساب كثافة المستويات الطاقوية(DOS) ومستوى الطاقة Et الخاص بالحصر(traps).

الكلمات المفتاحية *: الفوطوناقلية،الرش بيرولزي ، رقائق اؤكسيد الزنك،درجة حرارة، زمن الوضع، طريقة تحويل لابلاس*

ZnO thin film is widely used in the manufacture of the solar cells [1], optoelectronic [2], gaz detectors [3] and piezoelectrics devices [4]. Different techniques were employed for elaboration of these films as rf sputtering [5], chemical vapor deposition [6], ion beam assisted reactive deposition [7], thermal oxidation [8], and in particular spray pyrolysis technique [9]. This method is an inexpensive and simple technique, it has low toxicity and it does not require a high vacuum apparatus. Another advantage of spray pyrolysis technique is that the thin films can be deposited in air at different temperatures. Several works have done on the structure, the electrical, optical properties of these films. We are interested on the photoconductivity which informs us over the relaxation time and the density of states DOS, as well as others parameters.We have calculated these last using a numerical calculation developed by Studenikin [10].

II - EXPERIMENTAL TECHNIQUES

II-1 Deposition

The Zinc oxide thin films have been prepared by spray Pyrolysis. The solution used was the Zinc acetate dihydrated of concentration 0.2 mol/l dilute in pure methanol. We deposited on corning glass substrate, their temperature varied about 250 to 400°C. The deposition time was changed among 85s to 220s. The samples were illuminated by xenon spectral lamp of power 1000W/m2 during 20s. In table 1, the parameters as substrate temperature Ts, deposition time td and thickness were given.

Table 1 : Deposition parameters.

Sample	S2	S3	S5	S18
Ts (K)	523	573	673	523
Thickness (μm)	0.5	0.5	0.5	0.3
td(s)	220	220	220	85

II-2 X-Rays study

The samples were subsequently analyzed with X-rays Diffractometry techniques using a monochromatic radiation Cu K_α λ=1.5406 Å. The corresponding X-rays diffraction for different substrate temperatures Ts, in the range of scanning angle $30° < 2\theta < 70°$ are illustrated in figure1. The zinc oxide crystallizes in the wurtzite structure with lattice parameters a = 3.25 Å c = 5.12 Å. The average grain size cristallites l calculated using Scherrer's formula [11]. l varied from 160-400 Å. We notice that the preferential orientation depends upon deposition conditions. At high temperature, the peak (002) is high than (101). It means that the films grows preferentially with the (002) plane. The samples have random growth. This is evidenced by the presence of three peaks (001), (002) and (100). The same tendency was observed by other authors, results obtained agree with those reported by M.Yoshida, Studenikin, Ambient [7, 12-14].

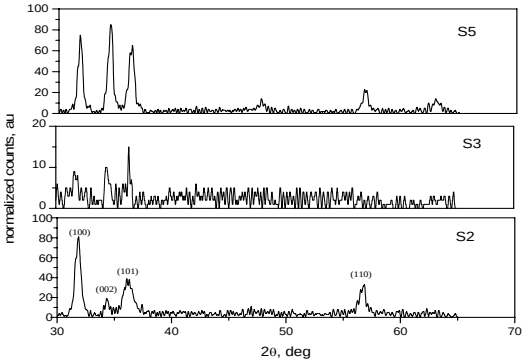

Figure 1 : X-rays diffraction spectra (effect of substrate temperatureTs).

The X-rays for differents deposition time td are depicted in figure2. We see that (100) is the preferential orientation. This orientation is weak for a low deposition. We have also (100), (002), (101),(110). The increasing deposition time improve the cristallinity of the ZnO thin films. This can be attributed to a high thickness [15].

Furthermore, the textural coefficients versus substrate temperatures were illustrated in figure 3 for three important peaks (002), (101) and (100). Hence these results confirm that the high peak depends on high temperature of substrate [12]

II-3 Optical band gap

II.3.1 Substrate temperature Ts effect. The absorption spectra are represented on figure 4. We assume that our samples exhibt high absorption (100%) in the U.V range.

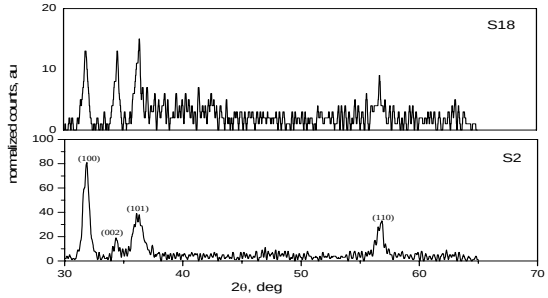

Figure 2: X-rays diffraction spectra (effect of deposition time td).

Then, it decreases for the wavelength range corresponding to violet –blue light. It is shown in figure 4 that the high substrate temperature improves the absorbance mainly in 300-400 nm range.

The variation of the squared absorption coefficient $(\alpha h\nu)^2$ versus the photon energy ($h\nu$) has been plotted in figure5. The energy gap is deduced by extrapoling the linear portion of the absorption spectra. The absorption coefficient versus incident photon energy $h\nu$ follows an empirical relation:

$$\alpha = \sqrt{h\nu - Eg} \quad (1)$$

The values of the gap obtained for different substrate temperatures are regrouped in table 2. Consequently, we have found the optical gap slightly small than the bulk value of 3.31 eV [12-14]. The effect of interaction electron-electron, defects and impurities leads to a reduction in the optical gap [14].

Table 2: Energy gap for different substrate temperatures.

Substrate temperature Ts (K)	523	573	673
Energy gap (eV)	3.3	3.16	3.26

II.3.2 Deposition time td effect. Figure 6 shows the optical spectra of the elaborated ZnO films for different deposition time at substrate temperature 523 K.

We may confirm that the growth of deposition time improve the absorption, due to high thickness [15].

Absorption coefficient versus photon energy is depicted in figure 7. The gap values are summarized in table 3

Table3: Gap Eg, effect of deposition time.

Samples	S18	S2
Deposition time td (s)	85	220
Gap Eg (eV)	3.26	3.30

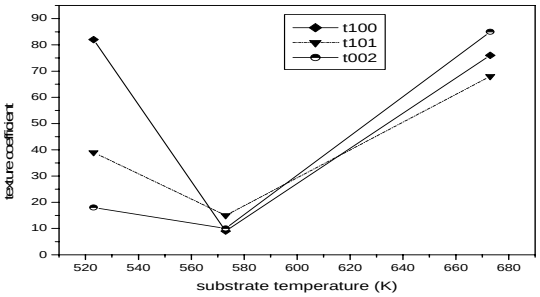

Figure 3 : Texture coefficient versus temperature Ts.

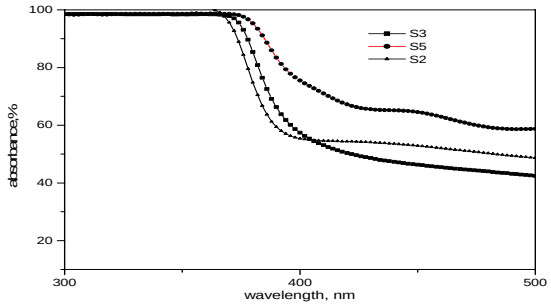

Figure 4: Absoption spectra (substrate temparature effect), td =220s.

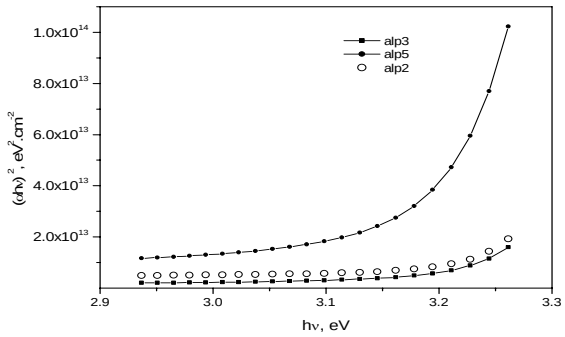

Figure 5 : Absorption coefficient for different substrate temperatures.

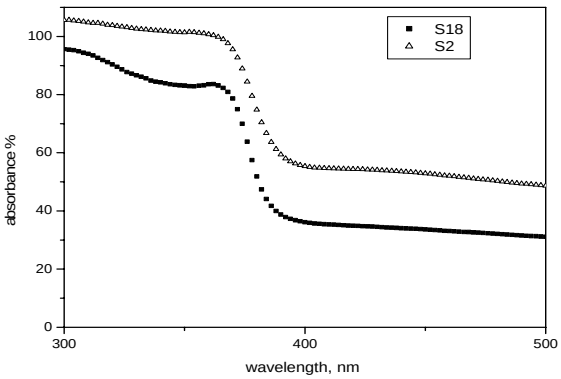

Figure 6: Absorbance versus wavelength.

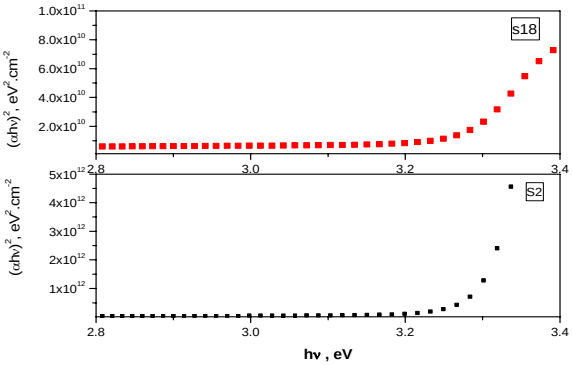

Figure 7: Absorption coefficient for different deposition time.

II-4 Electrical conductivity

The electrical conductivity σ was measured at room temperature. The variation of the conductivity of undoped ZnO with substrate temperature is illustrated in figure 8. The conductivity depended upon deposit parameters as time and temperature. We used air as carrier gas. So, an important number of oxygen molecules are chemisorbed in the film, both at the grain boundaries and on the surface. This caused a weak conductivity at low temperatures [14-15]. At high temperature, a larger grains size caused an increase of conductivity. The mobilty is proportional to l and this caused a large number of free electrons [13]. The measured values of conductivty are given in table 4.

Table 4: Conductivity and electron density.

Substrate temperatue Ts (K)	523	573	673	523
Deposition time (s)	220	220	220	85
Conduct. σ $(\Omega.cm)^{-1}$	0.06	0.02	0.6	0.008
Electrons density n (cm^{-3})	3.3 E +17	1.1 E+17	5.6 E+19	3 E+16

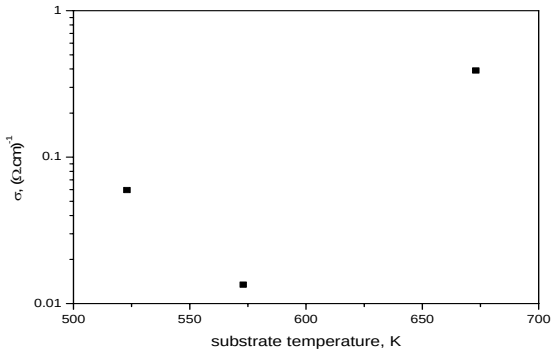

Figure 8: Conductivity σ versus temperature.

In polycrystallines films, the electrical properties are influenced by grain boundary effects. According to the model of Petriz [16], we supposes that the atoms in the grain boundaries are disordered compared to crystallites. It results a great number of defects which are corresponding to hanged bonds. Consequently, it is formed states of trap located in the forbidden band. The traps states are able to trap the carriers and to immobilize them what reduces the concentration of the free carriers. This involves the reduction in conductivity. Considering the model of Seto [17], where there is only one type of impurities uniformly distributed and completely ionized. The grain boundaries contain Nt localized traps which have energy level Et compared with the intrinsic level of Fermi. The traps are supposing neutral and become charged by the trapping of the carriers.

The Debye screening length can be calculeted from hydrogenic model. The expression is [13].

$$\frac{1}{L_D^2} = \frac{4n^{1/3}}{a_0} \qquad (2)$$

Where a_0 is the Bohr radius for the donor centres, ε is ZnO dielectric constant. It is given by:

$$a_0 = \frac{\eta^2 \varepsilon}{m^* e^2} \qquad (3)$$

From equations (2) and (3), we have :

$$L_D = (\eta / 2e)(m^* n^{1/3} / \varepsilon)^{-1/2} \qquad (4)$$

Calculated values of L_D which varied from 12 to 9 Å. So the condition $2L_D < l$ appropriate for a trapping model is verified.

II-5 Transient photoconductivity

By using the transient photoconductivity method, we determine the traps density and illustrate their variation versus substrate temperature and deposition time.

II.5.1 Temperature Ts effect

Figure 9 shows the photoconductivity versus time. We conclude that photoconductivity arise with substrate temperature. Illimunation caused a generation of paires electron–hole. Oxygen desorption is effected by capture of photogenerated hole by O_2^-. This increases electron density in the conduction band and then the photoconductivity. The decay is due to readsorption of oxygen. Absorbed oxygen captured an electron from the conduction band and became chemically absorbed, accompagnied by a decrease in photoconductivity [18-19].

For sample 3, the light off caused a continuous growth of photoconductivity. That can be to:

- The traps which retain for a long time the electrons.
- Defects, the impurities which tend to capture the electrons of the band of conduction.
- Time between the excitation and the recombination is rather long if the electrons traps are release gently towards the band of conduction.

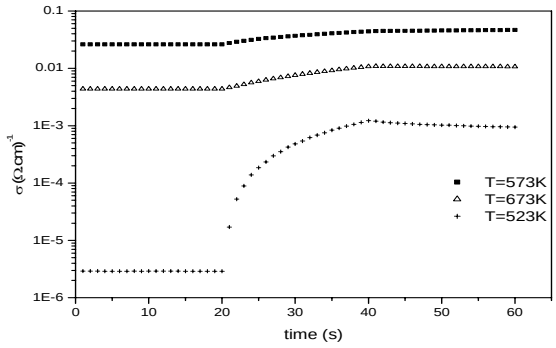

Figure 9: Photoconductivity versus time of undoped ZnO films. (Effect of substrate temperature).

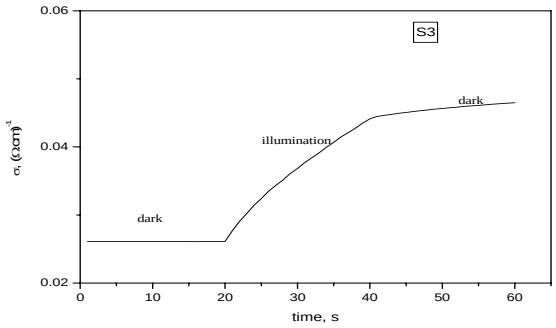

Figure 10: Photoconductivity versus time.

II.5.2 Effect of deposition time td

This effect is depicted on figure 11. Decay photoconductivity presents exponential variation.

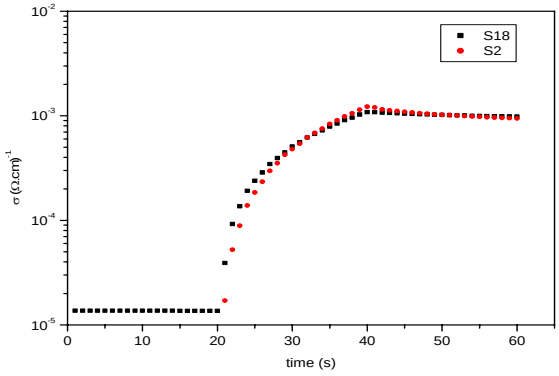

Figure 11: Photoconductivity versus time (effect of deposition time).

II.5.3 Calculus of traps DOS

The improved Laplace Transform method LTM is generaly applicable as a mean to obtain DOS, this method could be helpful for analysis of non-exponential transients photoconductivity. Hence, improved LTM has been used to calculate the density of states and the concentration of traps, and trap level in the gap by equations developed in following. n is the electron density, n_0 is the electron density at equilibrium, the main equations of LT method are given[10,20].

$$n = \sum_{i=1} Ni \exp(-t/\tau i) \quad (5)$$

By using the DOS g (E), the density n is giving by:

$$n = n_0 + \int g(E) \exp(-t/\tau(E)) dE \quad (6)$$

Where energy E = Et-Ev Et is the trap energy level above the valence band Ev.If the electron could escape from the trap, it will have then the probability :

$$\frac{1}{\tau} = \nu \exp(-E/kT) \quad (7)$$

Where the escape time τ (E) is given by:

$$\tau(E) = \frac{1}{\nu} \exp(E/kT) \quad (8)$$

ν is the escape frequency. This last means the lattice vibration frequency which equals to 1E+13 s^{-1}. The Laplace transform method with Laplace variable s is applied for transforming equation (5) to:

$$n = \frac{n_0}{s} + \int \frac{g(E)}{s + (1/\tau)} dE \quad (9)$$

$$\frac{d(sn)}{d(\ln s)} = s \int g(E) f(s,E) dE \quad (10)$$

in which the function f (s,E) is given by:

$$f(s,E) = \frac{\nu \exp(-E/kT)}{[s + \nu \exp(-E/kT)]^2} \quad (11)$$

The fitting procedure of the decay transient photoconductivity curve is used for determining relaxation time τ and electron density n(t) = σ(t) /μe. The gaussian form of DOS permits to find the trap density Ni which corresponds to area of the gaussian and their energy Et. The values of Ni, Et, and the relaxation time τ are on table 5. We can see distinctly the gaussian shape of the density DOS curve versus (Et-Ev) in the figure 12. The decrease in conductivity with decreasing td is caused by a largest density of localized traps. This attributed to change in grain orientation, to chemisorption effect and also to small grains size [13, 15]. The trap density approaches the value of 4.5 E+16. The substrate temperature effects on calculated DOS are represented in figure 13.

Table 5: Trap energy, relaxation time, trap density.

Samples	S18	S2	S5
Substrate Temperature Ts(K)	523	523	673
Deposition time t_d (s)	85	220	220
Relaxation time τ (s)	14.5	14.5	14.5
Traps density Ni (cm^{-3})	4.58 E+16	4.12 E+16	9.32 E+15
Trap energy Et (eV)	0.84	0.84	0.85

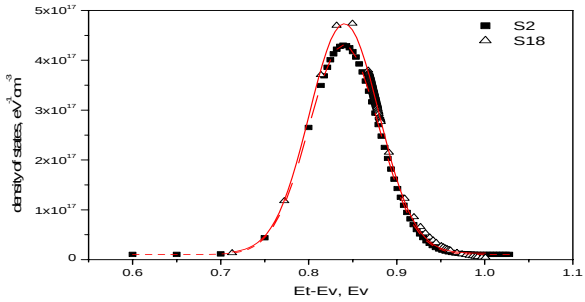

Figure 12: Density of states versus (Et-Ev).
Full squares td = 220s, triangular td = 85 s. Full and broken curves obtained by gaussian fitting.

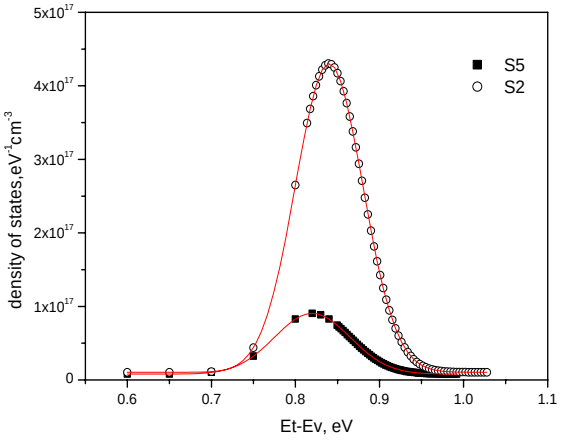

Figure 13. Density of states versus (Et-Ev).

(Open circles) Ts =523 K, full squares Ts = 673 K. Full curves obtained by gaussian fitting.

Values of traps density confirmed that high temperature improves the conductivity by a decrease **of** density traps. This behavior is due to desorption, and large grains. A preferential orientation is shown up [9, 8, 14].

CONCLUSIONS

In this work, the steady study of undoped ZnO thin films is divided in two parts, the experimental one and the simulation one. We may conclude that the parts are complementaries and achieve performances of these thin films. Substrate temperatures and time deposition have a considerable effect on the properties of undoped ZnO thin films deposited by spray pyrolysis. At high temperature the cristallinity and grain size are improved. In fact, XRays patterns show a preferential orientation which is c (002). The samples are entirely absorbants in UV range, then the absorbance decrease from 100 % to 50 % for the violet and blue light where λ varied from 395 to 490 nm, thus the thin films could be used in optoelectronic devices. Also the grain boundaries and chemisorption-desorption influenced the electrical properties because they trapped the electrons. For high substrate temperature electrical conductivity σ is around 0.6 $(\Omega cm)^{-1}$. The deep and steady work upon transient photoconductivity gave results as density Ni = 9.32^{E}+15 and energy traps Et = 0.85 eV, The annealing in suitable atmospheres and doping of the ZnO thin films could improve their properties.

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